Tetrahedron Letters Vol. 22, pp 155 - 156 0040-4039/81/0108-0155$02.00/0

PHOTOINITIATED SUBSTITUTION REACTIONS OF 2 AND 4-PYRIDINECARBONITRILE WITH CYCLOPENTENE

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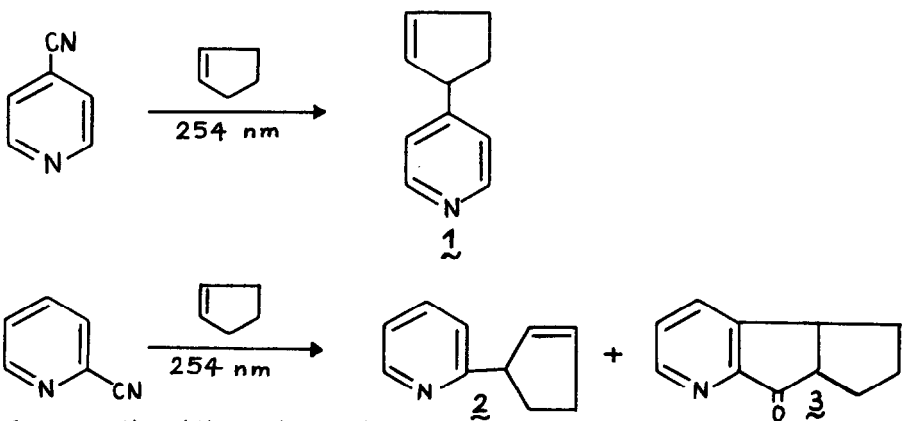
Summary: The photoreactions of 4 and 2-pyridinecarbonitrile with cyclopentene carried out in acetone or in acetonitrile solutions lead, respectively, to 4-(2 cyclopentenyl)-pyridine 1 and 2-(2 cyclopentenyl)pyridine 2. From 2-pyridinecarbonitrile a little amount of ketone 3 is obtained.

Recently a report on the reaction of 2-pyridinecarbonitrile with some olefins brings to the conclusion that the reaction involves addition to the cyano group with formation of annelated ketones only[1]. Furthermore no reaction was reported occuring with 4-pyridinecarbonitrile. Because we are active in the field of the photoreactions of cyano heteroaromatic bases[2], this claim prompts us to report our results on the same reactions that are partly in contrast with those reported[1].



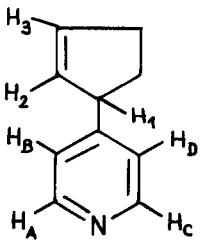
We find that 4-(2 cyclopentenyl)pyridine 1 is obtained when a solution of 4-pyridine-carbonitrile (1 mmole) and cyclopentene (5 mmole) in acetone or in acetonitrile (15 ml) is irradiated at 254 nm in a quartz vessel in a Rayonet RPR 100 photochemical reactor for 18 h. (yields 45% and 60% respectively). No other products are present in the reaction mixture. The product, as oil, was isolated after removal of solvent followed by preparative TLC or silica gel column (eluent: hexane-ethyl acetate 8:2) and characterized by NMR and mass spectra.

Furthermore when a solution of 2-pyridinecarbonitrile (1 mmole) and cyclopentene (5 mmole) in acetone (15 ml) is irradiated at 254 nm we obtained,in the same way,a liquid product (7%) characterized as 2-(2 cyclopentenyl)pyridine 2 (Table I).

The same reaction carried out in acetonitrile gives,after removal of solvent followed by preparative TLC (eluent:hexane-ethyl acetate 8:2) compounds 2 (23%) and 3 in a very little amount[3].

If,after irradiation, the reaction mixture is left to stand with water for several hours,or the irradiation was carried out in the same general conditions but with the presence of water (2 ml H_2O-15 ml acetonitrile) we obtained 2 (20%) and 3 (5%)[4].

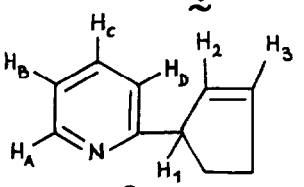
Table I. Spectral data of products



1

^{1}H NMR ($CDCl_3$): 8.5 δ (dd H_A and H_C, $J_{AB}=J_{CD}$=4.5 Hz), 7.15 δ (dd H_B and H_D, $J_{BA}=J_{DC}$=4.5 Hz, J_{BD}=1.8 Hz), 5.95 and 5.75 δ (m 2H: H_2,H_3), 3.87 δ (bs 1H:H_1), 2.42 δ (bs 4H)

MS m/e 145 (M^+)



2

^{1}H NMR ($CDCl_3$): 8.58 δ (dd H_A, J_{AB}=5 Hz, J_{AC}=2 Hz), 7.64 and 7.15 δ (m 3H:H_B,H_C,H_D), 6.02 and 5.88 δ (m 2H:H_2,H_3), 4.1 δ (bs 1H:H_1), 2.5 δ (bs 4H)

MS m/e 145 (M^+)

The photosubstitution reactions of cyano group by olefins leading to allyl derivatives appear to be the principal occuring reactions in all cases we checked (a wide range of cyano heteroaromatic bases and cyclic or aliphatic olefins[5]).

Studies are in progress to clarify the reaction mechanism.

References and Notes

† CNR-Centro di Studio per le Sostanze Organiche Naturali

(1) I.Saito,K.Kanehira,K.Shimozono,and T.Matsuura,Tetrahedron Lett. 21,2737 (1980)

(2) T.Caronna,S.Morrocchi,P.Traldi,and B.M.Vittimberga,JCS Chem.Commun. 64,(1979)

(3) NMR spectra of 3 is identical to that previously reported[1].

(4) From reaction mixture also 2 pyridinecarboxamide was isolated (5%).It was not possible to isolate any iminium compoun[1] from which ketone 3 probably derives.

(5) R.Bernardi,T.Caronna,S.Morrocchi,and P.Traldi,JCS Perkin I,in the press

(6) Uncorrected yields were calculated by GCL analysis.

(Received in UK 30 October 1980)